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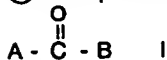
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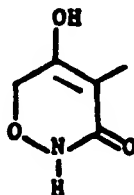
(54) Heterocyclic diones as pesticides and plant growth regulators.

(57) Compounds of the general formula I



wherein

A represents the group (i)



(i)

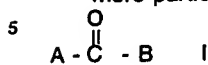
in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group are disclosed, as well as methods of producing such compounds, intermediates therefore, and their use as herbicides and acaricides.

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HETEROCYCLIC DIONES AS PESTICIDES AND PLANT GROWTH REGULATORS

The present invention concerns substituted 3,5-dioxo-3,4,5,6-tetrahydrooxazines as herbicides, processes and intermediates for their preparation, compositions containing them and their use as herbicides and acaricides.

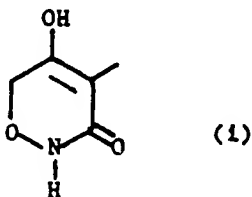
More particularly, the invention concerns compounds of formula I



wherein

A represents the group (i)

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in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group.

20

Examples of such B groups include phenyl, furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, dithiolyl, oxathiolyl, isoxazolyl, oxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, oxatriazolyl, dioxazolyl, oxathiazolyl, dioxinyl, pyridazinyl, pyrazinyl, triazinyl, oxazinyl, isoxazinyl, oxathiazinyl, morpholinyl, azepinyl, oxepinyl, thiepinyl, diazepinyl, benzofuranyl, isobenzofuranyl, benzothienyl, isobenzothienyl, thionaphthalenyl, isothionaphthalenyl, indolyl, isoindolyl, indazolyl, indoleninyl, isobenzazolyl, pyranopyrrolyl, isoindazolyl, indoxazinyl, benzoxazolyl, benzopyranyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinoxalinyl, quinazolinyl, naphthyridinyl, pyridopyridinyl, pyranyl, thiapyranyl, chromenyl, thiachromenyl, benzoxazinyl, benzisoxazinyl and purine.

25

Examples of substituents which may be present on ring (i) include alkyl, carboxy, alkoxy, carbonyl and phenyl, itself optionally substituted, or a spiro-ring. The hydroxy group may be substituted e.g. by alkyl, alkylcarbonyl, optionally substituted arylcarbonyl, alkoxy, aminocarbonyl (optionally substituted), alkylsulphonyl, phosphonyl (optionally substituted) phosphinyl (optionally substituted) or may form salts.

30

Examples of substituents which may be present on B include one or more alkyl, haloalkyl, alkoxy, haloalkoxy, halogen, nitro, cyano, alkyl S(O)_n, haloalkyl S(O)_n, cyanoalkyl S(O)_n, alkylsulphonyloxy, haloalkylsulphonylamino (including mono and dialkylamino), phenyl S(O)_n, benzyl S(O)_n, amino, alkylamino, dialkylamino, alkylcarbonyl, alkoxy, carbonyl, aminosulphonyl, alkylaminosulphonyl, dialkylaminosulphonyl, alkylcarbonylamino, alkylcarbonylalkylamino, formylamino, formylalkylamino groups. n is 0, 1 or 2.

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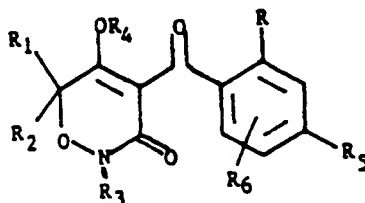
B is preferably phenyl, unsubstituted or substituted, as mentioned above.

USP 4,695,673 describes a wide range of acylated 1,3-dicarbonyl compounds and their use as herbicides but makes no reference to or suggestion of the 3,5-dioxotetrahydrooxazine ring characterizing the compounds of the present invention.

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A particular group of compounds of formula I is comprised of those of formula Ia

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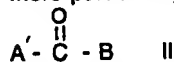


Ia

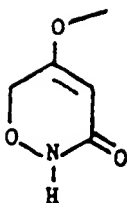
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wherein each of R₁, R₂ and R₃ is independently hydrogen, C₁₋₈alkyl, carboxyl, C₁₋₄alkoxy, carbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R₁ and R₂

- together form a C₂₋₆ alkylene bridge;
 R₄ is hydrogen, C₁₋₈ alkyl, C₁₋₈ alkylcarbonyl, C₁₋₈ alkoxy carbonyl, C(O)NR₇R₈, C₁₋₈ alkylsulphonyl, P(O)-(OR₉)(OR₉'), R₇P(O)-OR₉, benzoyl or a cation;
 R is C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms, C₁₋₈ alkoxy optionally substituted by 1 to 6
 5 halogen atoms, C₁₋₈ alkylcarbonyl, C₁₋₈ alkoxy carbonyl, NR₇'R₈', O_nS(O)_n'R₁₀, NR₇'SO₂R₈', halogen, cyano or nitro;
 each of R₅ and R₆ is independently hydrogen or selected from the meanings given for R; or
 R₅ and R₆ together form the group -Y-W-Z- with the proviso that R₅ and R₆ attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;
 10 each of R₇, R₇', R₇'', R₈, R₈' and R₈'' is independently hydrogen or C₁₋₈ alkyl;
 each of R₉ and R₉' are independently C₁₋₈ alkyl;
 R₁₀ is C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms;
 each of R₁₁, R₁₂, R₁₃ and R₁₄ is independently hydrogen, halogen or C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms;
 15 W is -(CR₁₁R₁₂)_t-(CR₁₃R₁₄)_{t'}- or sulphonyl;
 each of Y and Z is independently oxygen, sulphur, sulphonyl, CR₇'R₈'';
 n is 0 or 1;
 n' is 0, 1 or 2;
 t is 1 or 2; and
 20 t' is 0 or 1.
- In the above definitions, halogen is conveniently selected from chloro, bromo and fluoro, C₁₋₈ alkyl moieties, preferably have 1 to 4 carbon atoms.
- Each of R₁, R₂ and R₃ is preferably hydrogen, C₁₋₄ alkyl especially hydrogen or C₁₋₃ alkyl. Where R₁ and R₂ together form an alkylene bridge, it is preferably a C₃₋₆ alkylene bridge.
- 25 R conveniently signifies C₁₋₄ alkyl optionally substituted with halogen, -(O)_n-S(O)_n'-C₁₋₄ alkyl, halogen or nitro. It is preferably methyl, CF₃, C₁₋₃ alkylsulfonyl, C₁₋₃ alkylsulfonyloxy, chloro, bromo or nitro.
- R₅ is preferably bromo, chloro, fluoro, trifluoromethyl, SC₁₋₄ alkyl, OSO₂C₁₋₄ alkyl, SO₂C₁₋₄ alkyl, OSO₂C₁₋₄ haloalkyl, NR₇'SO₂C₁₋₄ alkyl, or, together with R₆, the group -Y-W-Z-. It is more preferably chloro, C₁₋₃ alkylsulfonyl or C₁₋₃ alkylsulfonyloxy, or, together with R₆, methylenedioxy.
- 30 R₆ is preferably hydrogen, C₁₋₄ alkyl, C₁₋₄ alkoxy, bromo, chloro or, together with R₅, the group -Y-W-Z-; it is more preferably hydrogen, methoxy or chloro, or, together with R₅, methylenedioxy.
- R₄ is conveniently hydrogen, C₁₋₄ alkyl, C₄₋₆ alkylcarbonyl, benzoyl, C₁₋₄ alkylsulfonyl or a cation. It is preferably hydrogen, methyl, ethyl, t-butylcarbonyl, isobutylcarbonyl, benzoyl or methylsulfonyl. As a cation R₄ is preferably an alkali metal such as Na⁺, K⁺, Li⁺ or an ammonium cation.
- 35 R₁ and R₂ are preferably H, C₁₋₄ alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R; more preferably H or C₁₋₃ alkyl e.g. H and methyl;
 R₃ is preferably C₁₋₈ alkyl, more preferably C₁₋₄ alkyl, e.g., CH₃ C₂H₅;
 R₄ is preferably H;
 R₁ is preferably NO₂, Cl, CF₃, more preferably NO₂ or Cl;
 40 R₅ is preferably Cl, Br, F, CF₃, SO₂-R₁₀, SR₁₀, OSO₂R₁₀, more preferably Cl, CF₃, OSO₂R₁₀, or SR₁₀, e.g., Cl, CF₃ or SCH₃;
 R₆ is preferably H;
 R₁₀ is preferably C₁₋₄ alkyl optionally halogen substituted, more preferably C₁₋₃ alkyl optionally halogen substituted, e.g., C₁₋₃ alkyl.
- 45 Preferred groups (i) are those in which R₁, R₂ and R₃ are each methyl and R₄ is hydrogen. Preferred groups B are those in which R₆ is hydrogen, R is nitro and R₅ is chloro or SCH₃. Two particularly preferred compounds are 2,6,6-trimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, and 2,6,6-trimethyl-4-(4-methylthio-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H, 6H)-dione.
- The compounds of the present invention of formula I are new substances which can be prepared by
 50 methods analogous to methods known in the art for the preparation of 2-aroyle-1,3-cycloalkyl-1,3-diones. More particularly, they can be obtained by, for example: rearranging an enol ester of formula (II)



wherein A' represents the group (ii)



(ii)

10 in which any free hydrogen may be replaced by an agriculturally acceptable substituent and B is as defined above to give a compound wherein the OH group in group (i) is unsubstituted (e.g. R_4 is H in compounds 1a).

This rearrangement is conveniently effected by reacting the compound of formula II with a cyanide source and a moderate base.

15 For example, the reaction may be carried out in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base. The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. 1,2-dichloroethane, toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide (DMF) and methyl isobutyl ketone (MIBK). In general, depending on the nature of the reactants and
20 the cyanide source, the rearrangement may be conducted at temperatures up to about 80 °C. In some cases, for instance when there is a possible problem of excessive by-product formation, the temperatures should be kept at about 40 °C maximum.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or
25 methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C_2 - C_5 aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin. The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. Generally about 1-10 mol % of the cyanide source is preferred.

30 By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this reaction include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as
35 triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate. The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 1.3-2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly, potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

40 Compounds of formula I where the OH group in the group (i) is substituted can be prepared by reacting a compound of formula I wherein the OH group in the group (i) is unsubstituted with either

a) the group R_{4O} -OH and a catalyst, or

b) the group R_{4O} -Q and a moderate base, wherein Q is a halogen atom, to give a compound of
45 formula I where R_{4O} is the desired substituent, e.g., one of the substituents defined for R_4 but excluding hydrogen.

The above reaction a) is carried out in the presence of a catalyst such as concentrated sulfuric acid. The reaction is conveniently carried out in a solvent which is also the reactant such as methanol, and at an elevated temperature.

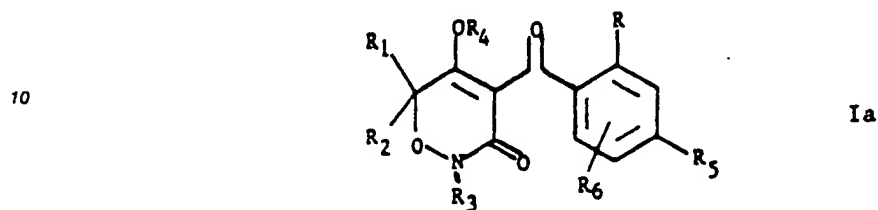
50 The above reaction b) is carried out in the presence of a moderate base such as triethylamine or pyridine and conveniently at RT or below.

The salt forms of compounds of formula I may be prepared by methods known per se, for example by reacting stoichiometric quantities of the compounds of formula I wherein R_4 is hydrogen with an appropriate base, for example, an alkali metal hydroxide, carbonate or bicarbonate, an alkaline earth metal hydroxide or carbonate, ammonia or an amine (e.g. diethanolamine, triethanolamine, octylamine, morpholine or dioc-
55 tylamine), in a suitable solvent. Acid addition salts of compounds of general formula I which incorporate an amino radical may be prepared from the corresponding compounds of formula I by methods known per se, for example by reacting stoichiometric quantities of the compound of formula I and the appropriate acid, for example an inorganic acid, e.g. hydrochloric acid, sulphuric acid, phosphoric acid or nitric acid, or an

organic acid, e.g. acetic acid, in a suitable solvent. The salts may, if necessary, be purified by recrystallisation from one, two or more suitable solvents.

The compounds of formula I may be recovered from the reaction mixture in which they are formed by working up by established procedures.

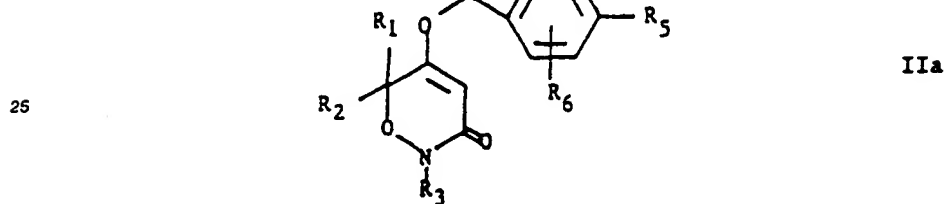
Under analogous conditions as described above, the compounds of the formula Ia



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wherein R-R₃, R₅ and R₆ re as previously defined may be prepared by
a) when R₄ is H, rearranging an enol ester of formula IIa

20



30

wherein R-R₃, R₅ and R₆ are as previously defined; or

b) when R₄ is as previously defined but excluding H, reacting a compound of formula Ia wherein R₄ is H and R-R₃, R₅ and R₆ are as previously defined with either

i) the group R₄-OH and a catalyst, or

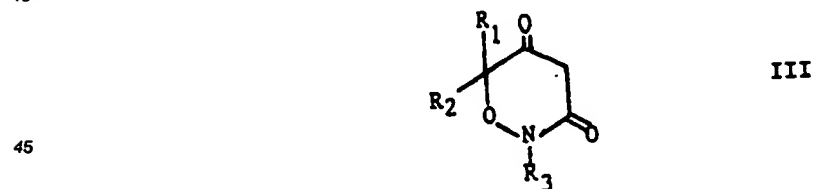
35 ii) the group R₄-Q and a moderate base, wherein Q is a halogen atom; and

R₄ is as previously defined but excluding H.

Similarly, the salt forms of compounds of formula Ia may be prepared according to the procedure described above for preparing the salt forms of the compounds of formula I.

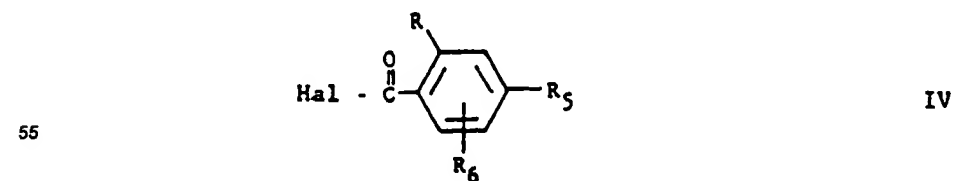
The compounds of formula IIa may be prepared by reacting a compound of formula III

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with a compound of formula IV

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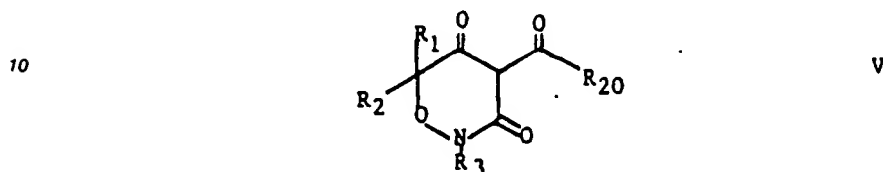


This reaction is carried out in the presence of a base such as triethylamine, potassium carbonate, pyridine, preferably triethylamine and in an inert solvent such as dichloromethane, acetonitrile, toluene, tetrahydrofuran, dimethylformamide. The reaction is conveniently carried out at RT or below.

The remaining compounds of formula II may be prepared analogously.

5 The compounds of formula III are new and also form part of the invention.

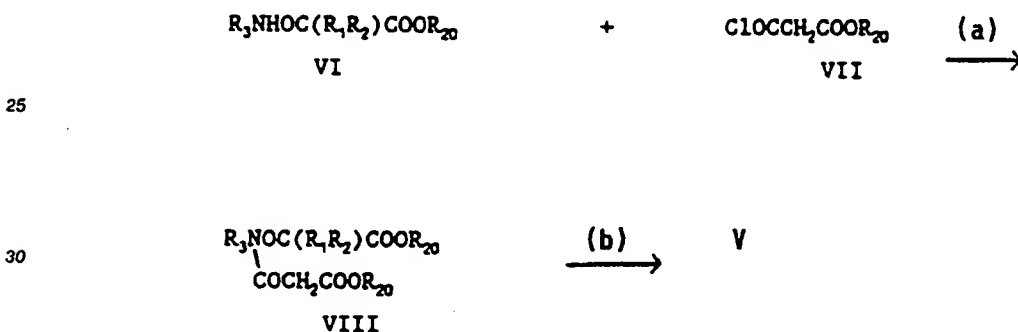
They may be prepared by decarboxylating a compound of formula V



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wherein R₂₀ is alkoxy, especially ethoxy or methoxy and R₁, R₂ and R₃ are as defined above. The reaction may be carried out at elevated temperatures e.g. 80-90° and in an inert solvent such as e.g. wet dimethylsulfoxide.

20 The compounds of formula V may be prepared analogously to known methods e.g. according to the following reaction scheme.



35 wherein R₁₋₃ and R₂₀ are as previously defined.

Reaction (a) may be carried out in an inert solvent such as dichloromethane and aqueous ether and in the presence of a base such as triethylamine or sodium carbonate at RT.

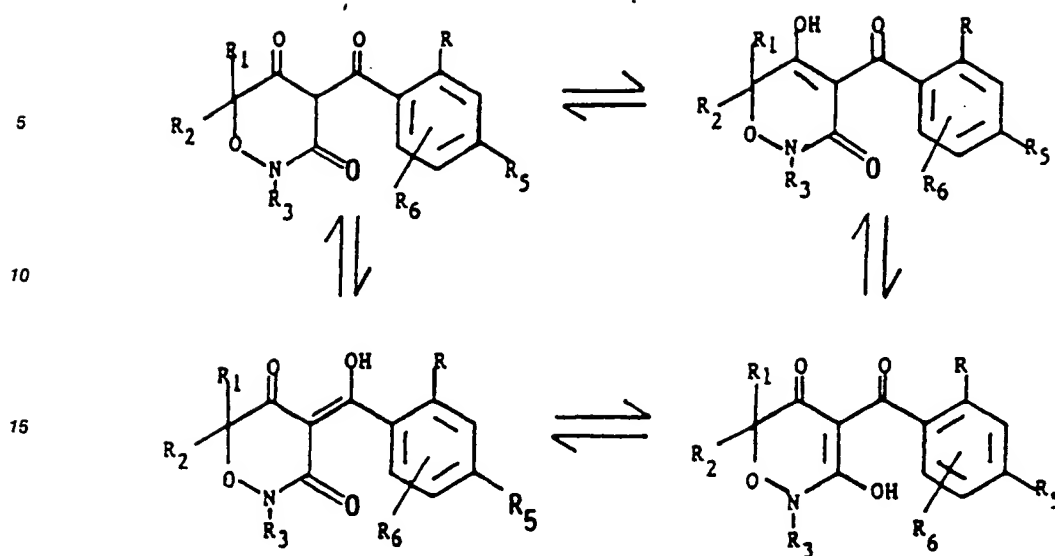
Reaction (b) may be carried out in an inert solvent such as toluene benzene or tetrahydrofuran in the presence of a base such as sodium methoxide or sodium hydride.

40 The remaining starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the processes described herein or to known processes [cf for compounds VI Kornowski et al. Bull. Soc. Chim France 1966(2)683].

45 The compounds of this invention wherein the OH group in group (i) is unsubstituted can have four structural formulae because of tautomerism as illustrated as follows for formula Ia where R₄ is H:

50

55



The novel compounds of formula I are useful for the control of weeds, using pre- and/or post-emergent treatments. Compounds of formula I are also useful as plant growth regulators (PGRs) and acaricides. The compounds can be applied in the form of dusts, granules, solutions, emulsions, wettable powders, flowables and suspensions. Application of a compound of the present invention as herbicides is made according to conventional procedure to the weeds or their locus using an herbicidally effective amount of the compounds, usually from about one-tenth or less to ten pounds per acre (0.11 or less to 11 kg/ha, e.g. 0.05 to 11 kg/ha) more usually 0.05 to 5 kg/ha, and preferably 0.1 to 1 kg/ha, the application being repeated as necessary. The application of a compound of the present invention to the "locus" of the weed includes application to the seeds, the plant (weed) or parts of the plant, or the soil.

Application of a compound of the present invention as an acaricide is made according to conventional procedure to the site of infestation using an acaricidally effective amount of the compound, usually 100 g/ha to 1 kg/ha.

The term "herbicide", as used herein, refers to an active ingredient which modifies the growth of plants because of phytotoxic or plant growth regulating properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

The compounds of the present invention, when applied as either post or pre-emergents, demonstrate high levels of herbicidal activity on broadleaf, grass and sedge weeds. They also exhibit selectivity in wheat (e.g. compound 6 in Table A); corn and cotton (e.g. compound 2 in Table A); and rice.

In the use of the compounds of formula I for combatting weeds and acari, a compound of formula I, or mixture thereof, can conveniently be employed as compositions in association with acceptable diluent(s) for application to the weed, acari or their loci. Such compositions also form part of the present invention.

Methods of preparing suitable formulations which can be used with a compound of the present invention are described in the literature along with suitable liquid or solid carriers. The optimum usage of a compound of the present invention is readily determinable by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot testing.

Suitable formulations contain from 0.01 to 99 % by weight of active ingredient, from 0 to 20 % of surfactant and from 1 to 99.99 % of solid or liquid diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms a composition generally contain between 0.01 and 25 % by weight of active ingredient. Lower or higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90 %, preferably between 5 and 80 % by weight of active ingredient.

Useful formulations of the compounds of formula I include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula I with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula I may be used in micro-encapsulated form.

The compounds of formula I can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the weeds, acari or their loci.

Agriculturally acceptable additives may be employed in the herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

5 "Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or
10 diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such xylene or an alcohol such as isopropanol, and for liquid application forms, e.g. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary acaricidal or herbicidal activity for broadspectrum weed control or compounds having antidotal, fungicidal, insecticidal or insect attractant activity.

15 Typical herbicidal composition, according to this invention, are illustrated by the following Examples A, B and C in which the quantities are in parts by weight.

EXAMPLE A

20

Preparation of a Dust

10 Parts of a compound according to this invention and 90 parts of powdered talc are mixed in a
25 mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the weed infestation.

EXAMPLE B

30

Preparation of Wettable Powder

25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine
35 silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium ligninsulphonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water before use to a spray liquor with the desired concentration.

EXAMPLE C

40

Preparation of Emulsifiable Concentrates (EC)

45 13.37 Parts of a compound according to this invention are mixed in a beaker with 1.43 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely anionic surfactants), 5.61 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely non-ionic surfactants), 23.79 parts of dimethyl formamide and 55.8 parts of Tenneco 500-100 (predominantly a mixture of alkylated aromatics such as xylene and ethylbenzene) until solution is effected. The resulting EC is diluted with water
50 for use.

The following Examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight.

FINAL COMPOUNDS

55

EXAMPLE I

Preparation of 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione (formula Ia wherein R_1 and R_3 are CH_3 ; R_2 , R_4 and R_6 are H; R is NO_2 ; R_5 is Cl; (Compound No. 1 Table A)).

3.65 g of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one is treated at r.t. with 3.06 ml of triethylamine and 0.3 ml of acetone cyanohydrin in 20 ml of acetonitrile (20 ml). After stirring overnight the solution is concentrated to a small volume and then taken up in dichloromethane and water. The combined extracts are washed with dilute HCl, brine, dried and evaporated to yield an oily residue. The crude product is recrystallized from ether to give crystalline 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, M.P. 127.5°C .

Proceeding analogously to Example Ia the following compounds of formula I are obtained.

TABLE A

Cpd	R_1	R_2	R_3	R_4	R	R_5	R_6	m.p.
1	CH_3	H	CH_3	H	NO_2	4-Cl	H	127.5°
2	CH_3	CH_3	CH_3	H	NO_2	4-Cl	H	105°
3	CH_3	CH_3	CH_3	H	Cl	4- SO_2CH_3	H	110°
4	CH_3	CH_3	CH_3	H	NO_2	4-Br	H	Foam
5	CH_3	CH_3	CH_3	H	NO_2	4- OSO_2CH_3	H	128°
6	CH_3	CH_3	CH_3	H	NO_2	4- SCH_3	H	$104-6^\circ$
7	CH_3	CH_3	CH_3	H	NO_2	4-F	H	137°
8	CH_3	CH_3	CH_3	H	NO_2	4- SO_2CH_3	H	124°
9	CH_3	CH_3	C_2H_5	H	NO_2	4-Cl	H	Foam
10	CH_3	CH_3	C_2H_5	H	NO_2	4- OSO_2CH_3	H	115°
11	CH_3	CH_3	CH_3	H	CF_3	4-F	H	86°
12	CH_3	CH_3	CH_3	H	NO_2	4- CF_3	H	$102-103.5^\circ$
13	CH_3	CH_3	CH_3	H	NO_2	4- $\text{SO}_2\text{CH}_2\text{Cl}$	H	
14	CH_3	CH_3	CH_3	H	NO_2	4- $\text{SO}_2\text{C}_2\text{H}_5$	H	
15	H	H	C_2H_5	H	NO_2	4-Cl	H	
16	H	H	$n\text{-C}_3\text{H}_7$	H	NO_2	4-Cl	H	
17	H	H	$n\text{-C}_4\text{H}_9$	H	NO_2	4-Cl	H	
18	H	H	$n\text{-C}_4\text{H}_9$	H	NO_2	4- CF_3	H	
19	CH_3	H	$n\text{-C}_3\text{H}_7$	H	NO_2	4-Cl	H	
20	CH_3	H	$n\text{-C}_3\text{H}_7$	H	NO_2	4- CF_3	H	
21	CH_3	CH_3	CH_3	H	NO_2	H	H	87.5°
22	CH_3	CH_3	CH_3	H	NO_2	OCHF_2	H	

NMR Spectra

Compound 4

^1H nmr (CDCl_3): δ 1.30, 1.53 (s,s,6H,C(CH_3) $_2$), 3.08, 3.38 (s,s,3H,NCH $_3$) 7.21 (d,1H,8Hz), 7.83 (dd,1H,8Hz), 8.33 (d,1H,2Hz-phenyl H)

Compound 9

^1H nmr (CDCl_3): δ 1.33, 1.53 (s,s,6H,C(CH_3) $_2$), 1.20 (m, 3H,NCH $_2\text{CH}_3$), 3.66 (m,2H,NCH $_2\text{CH}_3$), 7.28 (d,1H,8Hz), 7.66 (dd,1H,8Hz), 8.18 (d,1H,2Hz-phenyl H).

EXAMPLE 2

Preparation of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one (formula IIa, $R_1 = R_3 = \text{CH}_3$, $R_2 = R_6 = \text{H}$, $R = \text{NO}_2$, $R_5 = \text{Cl}$)

To a solution of 1.77 g of 2,6-dimethyl-2H-1,2-oxazine-3,4(4H,6H)-dione in 15 ml of dichloromethane containing 2.4 ml of triethylamine is added dropwise at 0°C solution of 2.72 g of 4-chloro-2-nitrobenzoyl chloride in 10 ml of dichloromethane. After the addition is complete, the reaction mixture is stirred at r.t. for one hour, then diluted with dichloromethane, washed, dried and evaporated to dryness to give the title compound.

EXAMPLE 3

Preparation of 2,6-dimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione (Formula III $R_1 = R_3 = CH_3$, $R_2 = H$)

5

4.9 g of an oily mixture of 2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione and 2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione is obtained e.g. as illustrated below is heated at $79^\circ C$ in 25 ml of DMSO and 0.9 ml of water for 3 hours. The reaction mixture is taken up in ether, poured into water and extracted thoroughly with ether. The combined extracts are dried and evaporated to give 2,6-dimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione.

10

The following two diones may be prepared analogously.

2,6,6-trimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione (Formula III $R_1 = R_2 = R_3 = CH_3$)

2-ethyl-6,6-dimethyl-2H-1,2-oxazine-3,5(4H,6H)-dione (Formula III $R_1 = R_2 = CH_3$, $R_3 = C_2H_5$).

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EXAMPLE 4

Preparation of 2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione and 2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione as a mixture.

20

To a suspended solution of sodium methoxide, freshly prepared from 694 mg of sodium metal and methanol, in 45 ml of toluene is added dropwise at r.t. a solution of 7.1 g of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate, in 10 ml of toluene. After completing the addition, the resulting mixture is stirred at r.t. for 24 hours. The reaction mixture is poured into ice-water and extracted with ether (discarded). The aqueous solution is then acidified with 10% aqueous HCL and extracted with dichloromethane. The combined extracts were dried and evaporated to dryness to yield an oily mixture of the title compounds.

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EXAMPLE 5

Preparation of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate

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To a solution of 5.32 g of methyl 2-methylaminooxypropionate in 50 ml of dichloromethane is added dropwise at $0^\circ C$ a solution of 6.62 g of ethylmalonyl chloride in 15 ml of dichloromethane. After the addition is complete, the resulting solution is stirred at $0^\circ C$ for additional one hour. The reaction mixture is poured into water, and extracted with ether. The combined extracts are washed with dilute HCL, brine, dried and evaporated to give an oily residue which is chromatographed on silica gel to yield oily methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate.

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NMR spectra for the compounds of examples 2 to 5.

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Example 2

1H nmr ($CDCl_3$): δ 1.47 (d, 3H, $OCH(CH_3)$), 3.20 (s, 3H, NCH_3), 4.81 (q, 1H, $OCH(CH_3)$), 6.15 (s, 1H, $=CHCO$) and 7.77, 7.97 (s, dd, 3H, phenyl H).

50

Example 3

1H nmr ($CDCl_3$): δ 1.43 (d, 3H, $OCH(CH_3)$), 3.30 (s, 1H, NCH_3), 3.53 (q, 2H, $OCCH_2CO$) and 4.40 (q, 1H, $OCH(CH_3)$).

55

Example 4

2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

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¹H nmr (CDCl₃): δ 1.50 (d,3H,OCH(CH₃)), 3.21 (s,3H,NCH₃), 3.93 (2,3H,OCH₃), and 4.73 (q,1H,OCH(CH₃)).

10 2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

¹H nmr (CDCl₃): δ 1.40 (t,3H,OCH₂CH₃), 1.48 (d,3H,OCH(CH₃)), 3.21 (s,3H,NCH₃), 4.41 (q,2H,OCH₂CH₃) and 4.73 (q,1H,OCH(CH₃)).

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Example 5

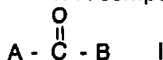
Methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate

20

¹H nmr (CDCl₃): δ 1.28 (t,3H,OCH₂CH₃), 3.23 (s,3H,NCH₃), 3.70 (q,2H,OCCH₂CO), 3.77 (s,3H,OCH₃), 4.21 (q,2H,OCH₂CH₃) and 4.57 (q,1H,OCH(CH₃)).

25 Claims

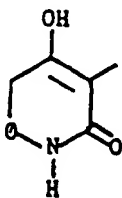
1. A compound of formula I



30 wherein

A represents the group (i)

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(i)

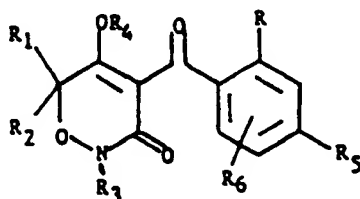
(i)

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in which any free hydrogen may be replaced by an agriculturally acceptable substituent; and B represents an optionally substituted aryl or heteroaryl group.

2. A compound having the formula Ia

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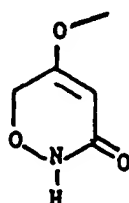
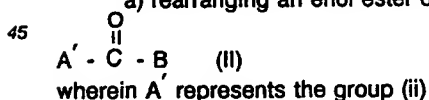
Ia

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55 wherein each of R₁, R₂ and R₃ is independently hydrogen, C₁₋₈alkyl, carboxyl, C₁₋₄alkoxycarbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R₁ and R₂ together form a C₂₋₆alkylene bridge;

R₄ is hydrogen, C₁₋₈alkyl, C₁₋₈alkylcarbonyl, C₁₋₈alkoxycarbonyl, C(O)NR₇R₈, C₁₋₈alkylsulphonyl, P(O)-

- (OR₉)(OR₉'), R₇P(O)-OR₉, benzoyl or a cation;
 R is C₁₋₈alkyl optionally substituted by 1 to 6 halogen atoms, C₁₋₈alkoxy optionally substituted by 1 to 6 halogen atoms, C₁₋₈alkylcarbonyl, C₁₋₈alkoxycarbonyl, NR₇R₈, O_nS(O)_n'R₁₀, NR₇'SO₂R₈', halogen, cyano or nitro;
- 5 each of R₅ and R₆ is independently hydrogen or selected from the meanings given for R; or
 R₅ and R₆ together form the group -Y-W-Z- with the proviso that R₅ and R₆ attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;
 each of R₇, R₇', R₇'', R₈, R₈' and R₈'' is independently hydrogen or C₁₋₈alkyl;
 each of R₉ and R₉' are independently C₁₋₈alkyl;
- 10 R₁₀ is C₁₋₈alkyl optionally substituted by 1 to 6 halogen atoms;
 each of R₁₁, R₁₂, R₁₃ and R₁₄ is independently hydrogen, halogen or C₁₋₈alkyl optionally substituted by 1 to 6 halogen atoms;
 W is -(CR₁₁R₁₂)_t-(CR₁₃R₁₄)_t' or sulphonyl;
 each of R₁₃ and R₁₄ is independently hydrogen, halogen or C₁₋₈alkyl optionally substituted by 1 to 6
- 15 halogen atoms;
 n is 0 or 1;
 n' is 0, 1 or 2;
 t is 1 or 2; and
 t' is 0 or 1.
- 20 3. A compound according to Claim 2, wherein
 each of R₁, R₂, R₃ is independently selected from hydrogen or C₁₋₄alkyl;
 R is selected from C₁₋₄alkyl optionally substituted with halogen, -(O)_n-S(O)_n'C₁₋₄alkyl, halogen or nitro;
 R₅ is selected from bromo, chloro, SC₁₋₄alkyl, OSO₂C₁₋₄alkyl, SO₂C₁₋₄alkyl, OSO₂-C₁₋₄haloalkyl, NR₇'SO₂C₁₋₄alkyl, or, together with R₆ the group -Y-W-Z-;
- 25 R₆ is selected from hydrogen, C₁₋₄alkyl, C₁₋₄alkoxy, bromo, chloro or, together with R₅, the group -Y-W-Z-;
 and R₄ is selected from H, C₁₋₄alkyl, C₄₋₈alkylcarbonyl, benzoyl, C₁₋₄alkylsulphonyl or a cation.
4. A compound according to Claim 2 wherein
 each of R₁ and R₂ is independently selected from H, C₁₋₄alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R;
 30 R₃ is C₁₋₈alkyl;
 R₄ is H;
 R is selected from NO₂ and Cl;
 R₅ is selected from Cl, Br, F, SO₂R₁₀, SR₁₀ and OSO₂R₁₀;
- 35 R₆ is H;
 and R₁₀ is selected from C₁₋₅alkyl optionally halogen substituted.
5. A compound according to Claim 4, wherein R₁, R₂ and R₃ are each methyl, R₄ and R₆ are each hydrogen, R is nitro and R₅ is chloro or -SCH₃.
6. A pesticidal composition comprising the compound of formula I or Ia as defined in Claims 1 or 2 to 5,
- 40 in association with an agriculturally acceptable carrier.
7. A method of controlling weeds comprising applying to the weeds or their locus a herbicidally effective amount of a compound of formula I or Ia as defined in Claims 1 or 2 to 5.
8. A process for preparing a compound of formula I as defined in Claim 1 which comprises
 a) rearranging an enol ester of formula (II)



(ii)

in which any free hydrogen may be replaced by an agriculturally acceptable substituent and B is as defined

in Claim 1 to give a compound wherein the OH group in group (i) is unsubstituted;

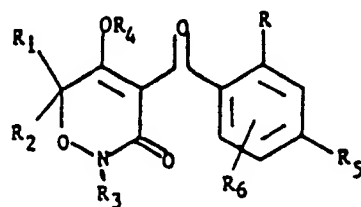
b) when the OH group in group (i) is substituted, reacting a compound of formula I wherein the OH group in the group (i) is unsubstituted with either

a) the group R_4 -OH and a catalyst, or

5 b) the group R_4 -Q and a moderate base, wherein Q is a halogen atom, to give a compound of formula I where R_4 is the desired substituent.

9. A process for preparing a compound of the formula Ia

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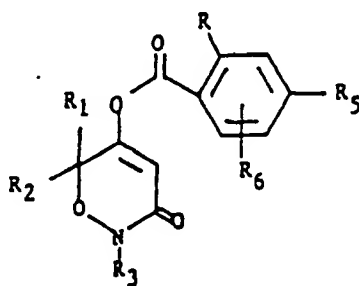
Ia

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wherein R - R_3 , R_5 and R_6 are as defined in Claim 2, which comprises

a) when R_4 is H, rearranging an enol ester of formula IIa

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IIa

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wherein R - R_3 , R_5 and R_6 are as defined above; or

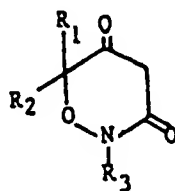
b) when R_4 is as defined in Claim 2 but excluding H, reacting a compound of formula Ia wherein R_4 is H and R - R_3 , R_5 and R_6 are as defined in Claim 2 with either

i) the group R_4 -OH and a catalyst, or

ii) the group R_4 -Q and a moderate base, wherein Q is a halogen atom and R_4 is as defined in Claim 2 but excluding H.

10. A compound of formula III

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III

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wherein R_1 , R_2 and R_3 are as defined in Claim 2.

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